

Crystallization and morphology of binary blends of linear and branched polyethylene: polarized light microscopy, small-angle light scattering and thermal analysis

J. M. Rego López* and U. W. Gedde†

Department of Polymer Technology, The Royal Institute of Technology,
S-100 44 Stockholm, Sweden

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The crystallization and morphology of binary 50/50 mixtures of branched polyethylene (copolymers based on butene-1, hexene-1 and octene-1; 0–1.3 mol%, $M_w \approx 65\,000$ – $146\,000$) and low molecular weight linear PE ($M_w = 2500$, $M_w/M_n = 1.15$) have been studied with differential scanning calorimetry (d.s.c), polarized light microscopy and small-angle light scattering (SALS). Crystallization kinetics were interpreted by applying the well-known expression: $G = G_0 e^{-U^*/R(T-T_\infty)} e^{-K_g/T\Delta T}$, where G = linear growth rate, G_0 , U^* , R and T_∞ are constants, T = crystallization temperature, ΔT = supercooling, f is a correction factor of about unity and K_g is related to the crystal surface energies and is determined from the kinetic data. The studied blends displayed two regimes of crystallization: at temperatures below 392.5 K, where both components crystallize in the same crystal lamellae (evidence is presented in a parallel paper), a remarkable low K_g value is obtained. A fine-textured spherulitic morphology is displayed in the samples crystallized at these temperatures. At temperatures higher than 392.5 K, where only the branched polyethylene component crystallizes, more perfect and larger spherulites are observed and a K_g value of about 125 000 is obtained which is in good agreement with what can be expected for regime II crystallization of samples of this molecular weight.

(Keywords: binary blends; linear polyethylene; branched polyethylene; crystallization; morphology; cocrystallization; polarized light microscopy; small-angle light scattering; thermal analysis)

INTRODUCTION

Linear and branched polyethylene have very similar chain structures, typically only different in one main chain carbon per hundred. These polymers are therefore excellent candidates for cocrystallization. Surprisingly few papers have, however, dealt with this scientifically and technically important topic^{1–9}.

Conventional (low pressure) branched polyethylene and linear polyethylene have been observed by thermal analysis to be largely incompatible in the solid state^{1,2}. Thermal analysis of blends of low, medium and high density polyethylenes has indicated that cocrystallization is possible when two of the components are close in branching content^{2–4}. Hu *et al.*⁷ studied binary mixtures of an ethyl-branched polyethylene with a linear polyethylene, both having a broad molecular weight distribution, by thermal analysis, X-ray scattering, Raman spectroscopy and small-angle light scattering (SALS). The presence of single melting, diffraction and scattering peaks in both slowly cooled and quenched samples was taken as evidence in favour of cocrystallization between these polymers. The authors of the papers cited consider the presence of a single, but often relatively broad, melting peak to be evidence in favour of cocrystallization. It has however been shown that a sample displaying unimodal melting may have two separate crystallite populations of the same melting temperature¹⁰. The

presence of a single melting peak in a sample should therefore be interpreted as a necessary but not sufficient condition for the existence of cocrystals.

Norton and Keller⁵, performing crystallization kinetics at 397 K and subsequent morphological studies by polarized light microscopy and transmission electron microscopy on a 50/50 blend of broad molecular weight linear and branched (1.4 mol% of ethyl groups) polyethylene, report a distinct segregation of the components. The linear polyethylene component crystallized first in a spherulitic morphology. The branched polyethylene component crystallized in the cooling phase and gave rise to fine-grained material which was located both inside and outside the large linear polyethylene spherulites. Crystallization at temperatures other than 397 K was not reported by these authors.

This paper deals with crystallization kinetics and morphology as revealed by polarized light microscopy, SALS and thermal analysis of 50/50 blends based on a low molecular weight linear polyethylene and different higher molecular weight branched polyethylenes. In a parallel paper¹¹, transmission electron microscopy data on the detailed lamellar organization in these samples are presented.

EXPERIMENTAL

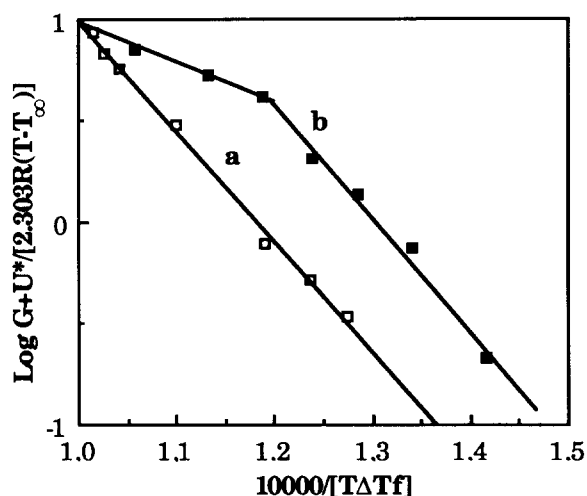
Binary 50/50 (w/w) mixtures of a linear PE sharp fraction ($M_w = 2500$, $M_w/M_n = 1.15$), referred to as L2.5, received from Polymer Laboratories Ltd, UK and different branched PE fractions (prepared from experimental

* Present address: Department of Physical Chemistry, Polymer Group, Basque Country University, Bilbao 644, Spain

† To whom correspondence should be addressed

Table 1 Molecular structure of branched polyethylene fractions

Sample	Branch	ϵ (%) ^a	M_w ^b	M_n ^b
BE1.3	Ethyl	1.3	84 000	33 000
BE0.5	Ethyl	0.5	146 000	76 000
BB0.4L	Butyl	0.4	64 000	10 000
BB0.4H	Butyl	0.4	125 000	32 000
BH0.8	Hexyl	0.8	94 000	40 000

^a Molar content of chain branches by i.r.^b By g.p.c.**Figure 1** Plots of $\{\log G + U^*/[2.303R(T - T_\infty)]\}$ vs. $1/[T\Delta Tf]$ for (a) BE0.5 (b) BB0.4L. The quantities used are defined in the Experimental section

LLDPE grades produced by Neste Polyethylene AB, Sweden and Dow Chemical Corp. (Dowlex 2049) by gel permeation chromatography (g.p.c.) at Rapra Technology Ltd, UK and described in Table 1) have been prepared by a solution mixing technique. Each binary mixture was made by stirring a hot *p*-xylene solution containing both components for at least 20 min, and then rapidly precipitating the polymer by adding an excess of cold methanol, followed by centrifugation, decantation and drying in vacuum to constant weight. G.p.c. analysis showed that the molecular weight distribution of the components in the blends were the same as prior to blending and that the blended samples indeed were 50/50 mixtures.

Crystallization kinetic studies have been carried out by polarized light microscopy (Leitz Ortholux POL BK II equipped with crossed polarizers and a temperature-calibrated Mettler Hot Stage FP 82) and d.s.c. (Perkin-Elmer DSC-2, temperature- and energy-calibrated according to standard procedures). The morphology of the crystallized samples was recorded by polarized light microscopy and SALS (H_v pattern, crossed polarizers).

Polarized light microscopy. Crystallization kinetic studies were performed in the hot stage by cooling (10 K min^{-1}) of the $10 \mu\text{m}$ thick samples from 450 K to the crystallization temperature (T) and photographic recording at different times (t) after the establishment of isothermal conditions. A linear relationship was in all cases established between the spherulite radius/axialite length and t . By measurement of at least five growing spherulites/axialites per sample at each temperature, a

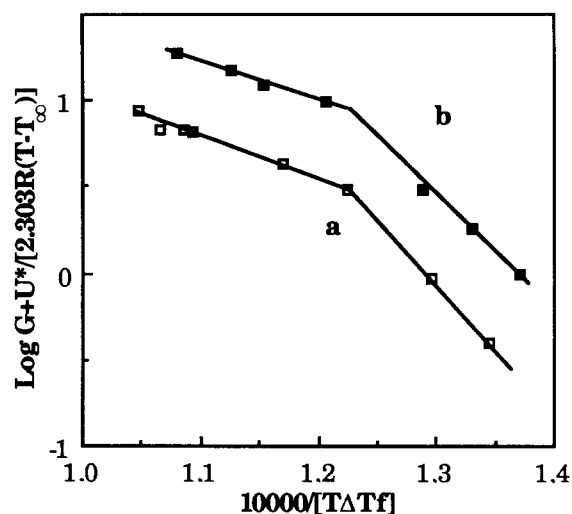
mean value for the linear growth rate (G) was determined. The linear growth rate data were further treated according to the equation derived by Hoffmann *et al.*¹³:

$$G = G_0 \exp[-U^*/R(T - T_\infty)] \times \exp[-K_b \sigma_e T_m^\circ / (k \Delta h_f T \Delta Tf)] \quad (1)$$

where G_0 is a constant, U^* is the activation energy for short range transport of crystallizable units, T_∞ is a temperature which is related to T_g , K is an integer constant which according to the theory¹³ is either 2 (regime II) or 4 (regime I), b is the monolayer thickness, σ is the lateral surface free energy, σ_e is the fold surface free energy, T_m° is the equilibrium melting temperature, Δh_f is the heat of fusion, ΔT is the supercooling and $f = 2T/(T_m^\circ + T)$, a correction factor taking into account changes in Δh_f with temperature. K_g , which is a frequently used notation, is defined as:

$$K_g = K_b \sigma_e T_m^\circ / (k \Delta h_f)$$

The thermodynamic data used in this paper are shown both at the end of the Experimental section and in the Results and Discussion section.

**Figure 2** Plots of $\{\log G + U^*/[2.303R(T - T_\infty)]\}$ vs. $1/[T\Delta Tf]$ for (a) BE0.5/L2.5 (b) BB0.4L/L2.5. The quantities used are defined in the Experimental section**Table 2** Equilibrium melting point values

Sample	T_m° (K) ^a	T_m° (K) ^b	$\langle n \rangle$
BE1.3	404.5	411	350
BE0.5	412.5	415	800
BB0.4L	411	415	800
BB0.4H	411	415.5	1000
BH0.8	408	414	600
L2.5	398	—	—
BE1.3/L2.5 ^c	405.5	410 ^d	—
BE0.5/L2.5 ^c	411	414 ^d	—
BB0.4L/L2.5 ^c	407	414 ^d	—
BB0.4H/L2.5 ^c	406	414.5 ^d	—
BH0.8/L2.5 ^c	407.5	413 ^d	—

^a From $T_m - T$ plot^b From theoretical calculation which is described in the text^c The equilibrium melting temperatures displayed in the table concern the branched polyethylene component^d Calculated from the temperature shift of $\log G$ vs. T data for the blend with respect to that of single-component branched PE

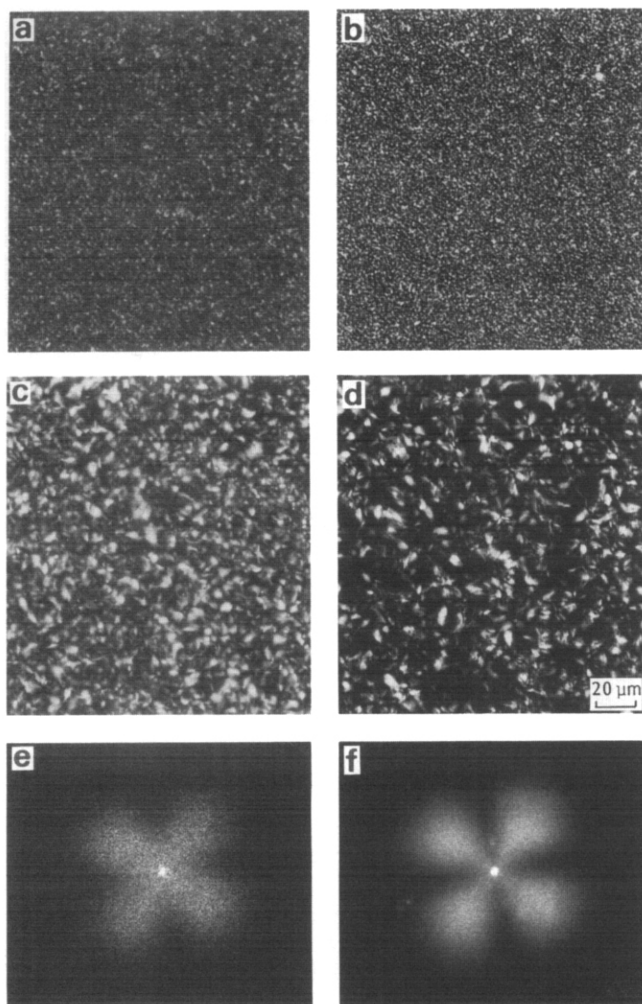


Figure 3 (a–d) Polarized photo micrographs of BE1.3/L2.5 crystallized at: (a) $T=387.6$ K; (b) $T=391.3$ K; (c) $T=392.4$ K; (d) $T=394.5$ K. Typical SALS H_v pattern for samples crystallized (e) in the LT region and (f) in the HT region

D.s.c. Samples weighing about 5 mg were cooled in the d.s.c. apparatus at a rate of 80 K min^{-1} from 450 K to the crystallization temperatures (T) after which isothermal conditions were established and the crystallization exotherm was recorded. The samples were finally cooled from T to 280 K at a rate of 80 K min^{-1} and then heated from 280 to 450 K while the melting was recorded. The crystallization data were treated according to equation (2) which is a d.s.c. equivalent of equation (1):

$$(t_{0.5})^{-1} = C \exp[-U^*/R(T - T_\infty)] \times \exp[-Kb\sigma_e T_m^\circ / (k\Delta h_f T \Delta T f)] \quad (2)$$

where $t_{0.5}$ is the time at which 50% of the final crystallinity is obtained and C is a constant. The other quantities used in equation (2) are defined under equation (1).

Thermodynamic data. $\Delta h_f = 293 \text{ kJ kg}^{-1}$ (ref. 12); $U^* = 6.3 \text{ kJ mol}^{-1}$ (ref. 13), $T_\infty = 201 \text{ K}$ (ref. 13), $\sigma = 14.1 \text{ mJ m}^{-2}$ (ref. 13), $b = 0.415 \text{ nm}$ (ref. 13).

RESULTS AND DISCUSSION

Equilibrium melting temperature

Any theory of crystallization requires knowledge of the

equilibrium melting temperature (T_m°). In this work two different strategies have been used to determine T_m° for the different samples: (1) by the extrapolation of melting temperature (T_m) – crystallization temperature data (T) data to $T = T_m^\circ$; and (2) by calculating the melting temperature of the equilibrium crystal assuming a random distribution of the chain branches on the main chain (eq. (3)), the complete exclusion of the chain branches from the crystals, i.e. the crystal thickness is controlled by the length of the segment between the branches, and the applicability of the Thomson-Gibbs equation (eq. (4)):

$$W(n) = n(1-p)^2 p^{n-1} \quad (3)$$

$$T_m = 418.1[(1 - 2\sigma_e)/(\Delta h_f \rho \langle n \rangle \langle \cos \phi \rangle l_{cc})] \quad (4)$$

where $W(n)$ is the weight fraction of unbranched chain segments with n carbons in the branched molecules with the branching probability per main chain carbon of $(1-p)$. An average value for n , denoted $\langle n \rangle$, of the crystallizing part of the sample was established on the basis of chain branching data (Table 1), equation (3) and d.s.c. crystallinity data. Notations used in equation (4): σ_e is the fold surface free energy, a value of 93 mJ m^{-2} (ref. 13) is used in the analysis, $\langle \cos \phi \rangle$ is the average cosine of the chain tilt angle, a value of 30° is used for ϕ and l_{cc} , the projected carbon-carbon bond length, is equal to 0.127 nm^{12} .

Data for both T_m° and $\langle n \rangle$ for the different samples are presented in Table 2. The T_m° values obtained from extrapolation of experimental $T_m - T$ data are generally markedly lower than those obtained from calculations based on method 2. The different values for T_m° for the different samples were applied to the linear growth rate data from polarized light microscopy via equation (1). The value of the fold surface free energy (σ_e) was calculated from the type of plot shown in Figure 1. The T_m° values obtained according to method 1 yield values for σ_e of about 30 mJ m^{-2} which is only 30% of the value expected^{10,13}. However, the σ_e values based on the T_m° data obtained by method 2 are in accordance with those obtained on linear PE of the same molecular weight (Table 3). In the subsequent analysis, T_m° is considered to be constant for each sample. It changes over the actual crystallization temperature range by only about 0.5 K.

Crystallization of branched polyethylene

The data presented in Figure 1 illustrate the two different trends obtained for the single-component branched PE samples: (1) BE0.5 exhibits data fitting well to a single line; (2) BB0.4L on the other hand yields two

Table 3 Crystallization kinetics of single-component branched PE

Sample	K_g^a (K^2)	K_g^b (K^2)	σ_e^a (mJ m^{-2})	σ_e^b (mJ m^{-2})
BE1.3	91 000(65 000)	– (59 000)	76(54)	–(50)
BE0.5	126 000(–)	97 000(–)	104(–)	81(–)
BB0.4L	130 000(64 000)	134 000(61 000)	108(53)	112(51)
BB0.4H	148 000(55 000)	146 000(82 000)	120(46)	121(69)
BH0.8	102 000(53 000)	139 000(81 000)	84(44)	117(67)

^a From polarized light microscopy according to equation (1) ($K=2$, T_m° according to Table 2)

^b From d.s.c. according to equation (2) ($K=2$, T_m° according to Table 2)

Values given are for the high temperature region; those in parentheses are for the low temperature region

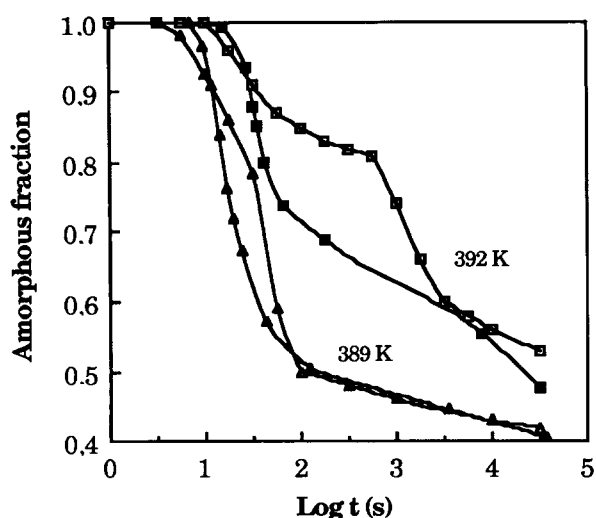


Figure 4 Amorphous fraction (by d.s.c.) vs. the logarithm of the crystallization time for BB0.4H/L2.5 crystallizing at 389 K (\blacktriangle) and 392 K (\blacksquare). The 'calculated' data curves (\triangle , 389 K; \square , 392 K) are based on crystallization data for the constituents treated according to equation (5)

lines with different slopes. The break point corresponds in this case to a degree of supercooling of 20 K. The actual values for σ_e corresponding to the low temperature region are too low by a factor of two assuming the validity of equation (1) with the K -values of 2. Polarized light microscopy data presented later in this paper show that spherulites are formed at temperatures on both sides of the breaking point. Thus, the high temperature crystallization should follow so-called *regime II* kinetics. For the determination of the fold surface free energy, it has therefore been assumed that K is equal to 2 (eq. (1)). Values of K_g and σ_e for these samples are presented in Table 3. These parameters have also been determined from d.s.c. data by application of equation (2) and it was found that the data obtained by d.s.c. are consonant with those obtained by polarized light microscopy. There is not only an excellent correspondence in the K_g values obtained (Table 3) but also in the temperature of the break point. The latter occurs at a supercooling of 21 ± 1 K for all the single-component branched PE samples studied. The K_g values recorded are somewhat greater (0–20%) than those reported in the literature. A very small decrease in T_m (≈ 1 K) would however suffice to decrease the K_g value to the expected level.

The existence of low temperature region crystallization with a K_g value of about 60 000 has not been reported before. The elucidation of this 'new' type of crystallization requires further experimental and theoretical work and will not be discussed further in this paper. The occurrence of regime I crystallization has not been critically controlled in our studies. Regime I crystallization occurs, according to experimental data and predictions from theory¹³, at supercoolings of less than 16.5 K which corresponds to 395 K for BE1.3 and 398–399 K for the other samples. Too few data points have been obtained in this temperature range to constitute a sound basis for declaring that regime I crystallization occurs in these samples.

Crystallization of linear/branched PE blends

Data from studies of the crystallization kinetics and morphology of the blends are presented in Figures 2 and 3

and Table 4. These data are obtained by equations (1) and (2) using the T_m values of the branched PE components according to Table 2. There are two different regimes of crystallization, referred to in this paper as 'high temperature' (HT) and 'low temperature' (LT). The transition between the two is very sharp and occurs over a temperature range smaller than 1 K (Figures 2 and 3). The following features are characteristic of the two crystallization types:

The HT crystallization is characterized by a K_g value of 120 000 (Table 4) and it occurs at temperatures greater than 392.5 ± 0.5 K for all the blends studied. This temperature constitutes the upper temperature for the crystallization of L2.5. Assuming that regime II crystallization occurs ($K=2$ in eqs. (1,2)) a value of about 100 mJ m^{-2} is obtained for σ_e (Table 4). Polarized light microscopy and SALS indicate that comparatively large and more perfect spherulites are formed at these temperatures than are formed at lower temperatures (LT domain) (Figure 3).

The LT crystallization is characterized by a K_g value which is only about 50 000 (Table 4). Small and less perfect spherulites are formed at these temperatures (Figure 3). Transmission electron microscopy data presented in a parallel paper¹¹ clearly show that cocrystallization occurs between the linear and branched PE components at these temperatures.

The theoretical background explaining the occurrence of the so-called LT crystallization, which involve cocrystallization of linear and branched polyethylene is dealt with in a subsequent paper¹⁵.

Figure 4 shows the typical crystallization behaviour (isothermal conditions) of the 50/50 blends in comparison with a reference blend of the two components of the 50/50 blend. The crystallization kinetics of the reference blend is calculated on the basis of crystallization data of the pure constituents according to equation (5):

$$W_c(t) = [W_{c1}(t) + W_{c2}(t)]/2 \quad (5)$$

where W_c , W_{c1} and W_{c2} are the crystalline weight fractions at time t of the blend, and of constituents 1 and 2, respectively.

The 'steps' which appear in the calculated curves presented in Figures 4 and 5 correspond to crystallization of the branched component and L2.5, respectively. The latter crystallizes more slowly at the temperatures used in the studies.

The blend BB0.4H/L2.5 crystallizes at all the temperatures studied to a final crystallinity in accordance with

Table 4 Crystallization kinetics of blends of linear and branched PE

Sample	K_g^a (K^2)	K_g^b (K^2)	σ_e^c (mJ m^{-2})	σ_e^d (mJ m^{-2})
BE1.3/L2.5	94 000(63 000)	100 000(43 000)	80	84
BE0.5/L2.5	140 000(54 000)	120 000(66 000)	116	99
BB0.4L/L2.5	140 000(44 000)	120 000(51 000)	116	100
BB0.4H/L2.5	140 000(18 000)	106 000(62 000)	116	88
BH0.8/L2.5	125 000(48 000)	130 000(64 000)	104	109

^a From polarized light microscopy according to equation (1) (T_m according to Table 2)

^b From d.s.c. according to equation (2) (T_m according to Table 2)

^c From polarized microscopy according to equation (1) ($K=2$)

^d From d.s.c. according to equation (2) ($K=2$)

Values are for the high temperature region; those in parentheses are for the low temperature region

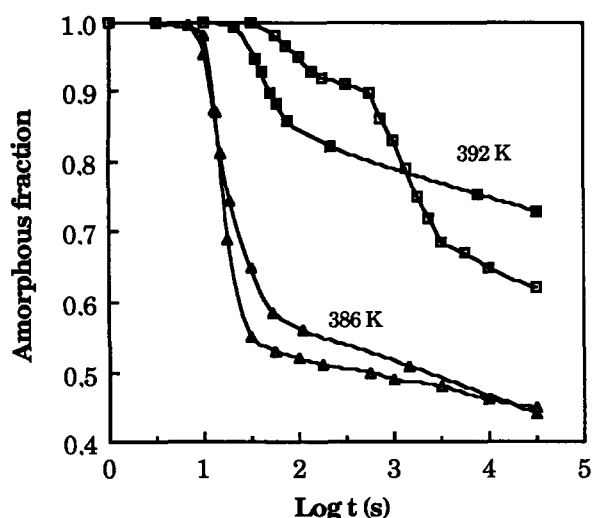


Figure 5 Amorphous fraction (by d.s.c.) vs. the logarithm of the crystallization time for BH0.8/L2.5 crystallizing at 386 K (\blacktriangle) and 392 K (\blacksquare). The 'calculated' data curves (\triangle , 386 K; \square , 392 K) are based on crystallization data for the constituents treated according to equation (5)

equation (5) (Figure 4). This behaviour is typical of the blends containing a branched polyethylene component with a low degree of chain branching, i.e. BB0.4L, BB0.4H and BE0.5.

The BH0.8/L2.5 blend crystallizes to a final crystallinity which at the lower temperatures is in accordance with the calculated degree of crystallinity obtained for the constituents, see equation (5). At higher temperatures, the measured final crystallinity is significantly lower than the corresponding calculated value (Figure 5). This kind of behaviour is typical for the blends which contain a highly branched polyethylene component, i.e. BB0.8 and BE1.3. We assume that the conditions for crystallization of L2.5 at the highest temperatures (392 K in Figure 5) are affected to a considerable extent by the presence of a significant fraction of highly branched material. The presence of a highly branched fraction in branched polyethylene is experimentally established¹⁴ and also indicated by predictions based on the assumption that the chain branches are statistically distributed on the chains (cf. eq. (3)). The highly branched material acts at these temperatures as a solvent for the lower molecular weight species of L2.5 which are prevented from crystallizing at these temperatures.

It is typical of all blends that the onset of crystallization is somewhat delayed in comparison with the single-component branched PE crystallization. The introduction of L2.5 delays crystallization of the branched component possibly by decreasing the equilibrium melting point of the latter. The shift to shorter times of the major part of the measured curves as compared with the calculated curves (Figures 4 and 5) does indicate that the crystallization of L2.5 is generally significantly promoted in the blends. This may be due to either epitaxial growth of crystals of L2.5 on the early formed crystals of the branched component or to cocrystallization of the components. Transmission electron microscopy data

presented in a parallel paper¹¹ clearly shows that cocrystallization occurs in the blends.

CONCLUSIONS

Crystallization kinetics and morphology studies of binary mixtures of low molecular weight linear PE ($M_w = 2500$, $M_w/M_n = 1.15$) and branched polyethylene (ethyl-, butyl- and hexyl-branched, 0.4–1.3 mol%, $M_w \approx 65\,000$ – $146\,000$) show the presence of two distinctly different crystallization types:

- (1) at temperatures higher than 392.5 K, where only the branched component crystallizes, a *regime II* crystallization occurs and a spherulitic texture is displayed;
- (2) at temperatures lower than 392.5 K, where both components crystallize, a microspherulitic morphology is obtained and crystallization occurs with a K_g value which is lower by a factor of two to three than the expected value for regime II crystallization. The K_g values have been calculated according to equations (1) and (2) using the T_m° values of the branched PE components. Electron microscopy on samples crystallized at these temperatures, presented in a parallel paper¹¹, indicate the occurrence of cocrystallization of the components. D.s.c. data are consistent with the above view, and demonstrate a strong 'interaction' between the components.

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